The Cracking of Petroleum Oils

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN

By
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1926

Easton, Pa.:
Mack Printing Company
1926

Ann Arbor
1926

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[Reprinted from Industrial and Engineering Chemistry, Vol. 18, No. 8, page 776, August, 1926.]

The Cracking of Petroleum Oils[1]

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A CRACKING apparatus has been developed permitting study of the individual variables, temperature, pressure, time, effect of nature of oil cracked, and effect of removal or nonremoval of gasoline as formed.

Cracking has been shown to be slow at 700° F. but rapid at 800° F. The cracking reaction rate doubles for an increase of 22° F.

Gasoline formation is a straight-line function of time, with two exceptions that are discussed in detail. With these same two exceptions the formation of gasoline can be regarded and formulated as a reaction of the first order.

The over-all process of cracking is extremely complicated and involves reactions both of decomposition and synthesis. Within the limits of error of these experiments, pressure, as such, has been shown to have no effect on the yield of gasoline. Several indirect effects of pressure are discussed. The unsaturation of gasoline is affected by pressure only when pressure indirectly affects the time that the gasoline stays in the reaction vessel. Unsaturation decreases with time of heating. Pressure, as such, has no effect on the boiling range of the gasoline produced in cracking.

Excluding experiments involving limited cracking only, heavy fuel oil cracks most easily, gas oil nearly as readily, but thermolized gas oil or "cycle stock" only 0.40 to 0.47 as rapidly. Removal of gasoline as formed has no effect either on the yield or boiling range of the gasoline produced. It does affect the unsaturation of the gasoline somewhat. Rates of pressure rise during cracking of three oils in a bomb, the relationship between specific gravity and extent of cracking, and the boiling ranges of gasolines produced by cracking under various conditions are given.

An apparatus for studying the thermal relations in cracking was developed and cracking has been shown to be endothermic to the extent of not over 500 calories per gram of gasoline produced.

Cracking is not a process in which an equilibrium state is reached as is somewhat commonly believed. The apparent state of equilibrium reached in cracking systems using lagged reaction chambers is the result of decreased reaction rate caused by the lowered temperature resulting from heat loss and endothermic cracking reactions.

THE cracking of petroleum oils for the production of gasoline is the outstanding development of the last decade in petroleum technology, and is, furthermore, an achievement of such social and economic importance as to rank with the really great industrial advances of all time. Gasoline of superior quality has been made available at prices well within the reach of all. To this end manufacturers have invested hundreds of millions of dollars in cracking equipment, thereby permitting operations that have exerted a profound stabilizing influence on the entire petroleum industry.

In view of the magnitude of the expenditure involved and the scale on which operations have been conducted, it is odd, indeed, that so little scientific work has been done to establish a foundation of fact on which the engineering superstructure might securely rest. Yet careful review[2] of the existent technical literature discloses little dependable definite information. Much that has been done and described is unreliable because of failure to control the individual variable factors.

The purpose of the investigation the results of which are here reported was, in part, to determine quantitatively, or as nearly quantitatively as possible, the effect of the fundamental variables in cracking—namely, temperature, pressure, time, and composition or nature of the oil cracked—and further to ascertain the effect of removal or nonremoval of the gasoline as formed, to determine the quality of the gasoline produced under various conditions, and to measure the heat absorbed or evolved in the over-all process of cracking. These are the most important and fundamental points on which information is necessary for the intelligent layout of a cracking procedure and the design of the equipment for its accomplishment.

As is almost invariably true, the more important processes used industrially have been in the main correct in principle. Day-to-day operation is an accurate, if slow, guide to the truth. Yet misconceptions exist and much money has been spent in the construction of ill-designed equipment. Also, the basic ideas of processes in current use are sufficiently

[1] Presented under the title "Cracking Liquid Petroleum Oils" before the Division of Petroleum Chemistry at the 71st Meeting of the American Chemical Society, Tulsa, Okla., April 5 to 9, 1926.

[2] Leslie, "Motor Fuels, Their Production and Technology," 1923, p. 270.

different to make an analytical study of commercial processes, in the light of quantitative data on the effect of the several variables, most interesting. Data of value in this connection are here presented. The analytical application is left to those concerned.

Experimental Procedure

To permit study of the effect of individual variable factors an apparatus of special construction was evolved (Figure 1). The more important requirements were quick heating of the oil to prevent extensive cracking while reaching the operating temperature, balancing of heat loss and gain from the cracking vessel to eliminate the film or layer of superheated oil always present next a vessel wall through which heat is flowing, ability to withstand a working pressure of at least 2000 pounds per square inch, and convenient arrangements permitting withdrawal of liquid or vapor, admission of inert atmospheres, and measurement of temperature and pressure.

In making an experiment, a charge of oil of approximately 2 gallons was placed in the chamber *A*, heated internally by an immersed resistance coil, *B*, and externally by two gas burners. A special hot-oil pump, *C*, circulated the oil rapidly over the heating surfaces in and of chamber *A*, thus bettering the heat transfer and decreasing the temperature and thickness of the superheated oil films. When the oil reached a temperature, read by thermocouple *D*, 50° F. above that desired during the experiment, it was rapidly transferred to a strongly built bomb, *E*, already heated to 50° F. above the desired running temperature. In passing from *A* to *E* the oil was cooled by the piping and heavy hydraulic valves through which it flowed. However, by proceeding in the manner described the final result was that bomb *E* was filled to the level of pipe *G* with oil at the proper temperature. The total volume of oil so taken was approximately 3000 cc.

The bomb *E* was housed in an insulating vessel provided with a layer of resistance coils on its inside surface, from which energy was radiated and conducted at a rate just sufficient to balance the heat loss from the bomb and to maintain the oil in the bomb at the desired temperature for the required time. Provision was made to read the pressure and temperature of the oil within the bomb.

A thermocouple, *H*, of No. 30 chromel-alumel, was carefully peened into the wall of the bomb in order to be able to determine the temperature difference between the metal of the bomb and the bulk of the oil. This is a direct measurement of any possible film superheat. Although the task of arranging a thermocouple to give the true temperature of a metal wall is difficult, this particular manipulation had been the matter of detailed study in connection with other apparatus and it is believed that the couple used here gave actual temperatures. In any event, the true temperature would be below that read from the couple, and since the temperature of the oil in the bomb and the steel wall of the bomb never differed by more than 10° F., except in occasional instances when coke formed and the difference rose to 15° F., the effect of oil film superheat can be entirely disregarded. The cracking reactions are effected isothermally throughout a homogeneous body of oil. This is extremely important.

After filling bomb *E*, the remainder of the oil in vessel *A* was drawn through cooler *J*, and the starting time of the run noted. Draining this residual oil, which constituted the blank sample of the run, required about 2 minutes.

The oil in bomb *E* was held at constant temperature for the required time, and a log of oil temperature, wall temperature, and pressure taken. At the conclusion of the cracking period the oil was discharged from the bomb through pipe *F* by autogenous pressure, and passed through ice cooler *J*, which cooled it to 120° F. or less. Auxiliary ice cooler, *K*, was used further to cool gas and vapor passing cooler *J*. The draining of bomb *E* required about 2 minutes. The bomb was finally flushed with nitrogen introduced at *L*, to remove residual gasoline vapor.

When vapor was to be removed during the run the thermocouple *I* was raised and a tee inserted. A valve between this tee and cooler *J* permitted accurate control of the pressure.

Analytical Distillations

The analytical distillations of blank and run samples were all made by use of an apparatus fractionating so closely as to give the true boiling point curve. The laboratory column used has been described by Peters and Baker.[3] These analyses are designated in the tables as Standard Column analyses. Other analyses, marked A. S. T. M., are made by the use of the A. S. T. M. standard apparatus for gasoline distillation.

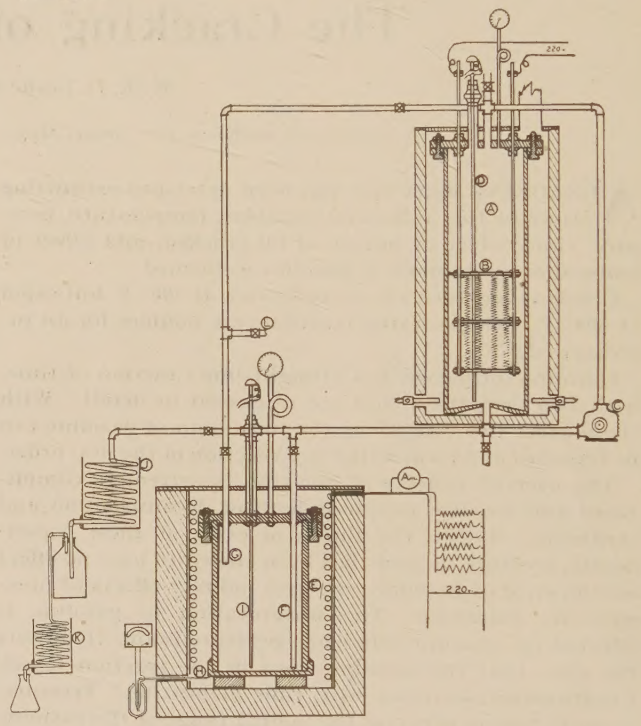

Figure 1—Cracking Apparatus

Standard column analyses check within ±0.5 per cent. Cutting at 450° F. vapor temperature in the standard column apparatus results in a gasoline product of approximately Federal Specification end point—that is, 437° F. apparent temperature or 444° F. true temperature.

Selection of Oils to Be Cracked

Three main classes of oils are cracked industrially—namely, gas oils or distillate oils, residuums or residual oils, and "cycle" stocks, or once-cracked oils. Guided by this, three oils were used in this work—a residuum comprising the heavier 50 per cent of a 37° A. P. I. Midcontinent crude petroleum; a gas oil from this same crude, but which was fractionated to remove part of the material boiling below 444° F., and also the highest boiling part of the gas oil as purchased; and a gas oil made by distilling a Dubbs process coke carrying residual oil. The properties of these three oils are given in Table I.

Careful consideration was given to the use of single pure hydrocarbons, or closely fractionated selected cuts, but it was decided that the information to be secured would be of greater

[3] This Journal, **18**, 69 (1926).

value if typical commercial oils were used. Furthermore, the fact that several hundred gallons of each oil were required practically precluded the use of individual hydrocarbons.

Table I—Properties of Oils Cracked

	Fractionated gas oil	Heavy fuel oil	Thermolized gas oil
Specific gravity, 60°/60° F.	0.8500	0.9070	0.9311
Sulfuric acid absorption, per cent	7.0	....	22.0
Per cent gasoline (material below 450° F. vapor temperature on standard column)	9.3	6.3	10.5
A. S. T. M. Distillation			
	° F.	° F.	° F.
F. D.	415	410	270
10	500	515	499
20	527	581	569
30	553	650	610
40	574	696	640
50	593	720	669
60	616	Cracking	698
70	638	...	728
80	663	...	765
90	703	...	...
95	737	...	...

Criterion of the Extent of Cracking

As a criterion of the extent of the reactions which over all are called "cracking," the volumetric percentage of distillate below 450° F. vapor temperature in the standard column apparatus was used. This is really the volumetric percentage of Federal Specification 437° F. end-point distillate.

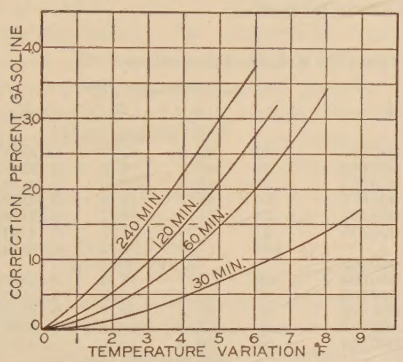

Figure 2—Temperature Correction Curves for 800° F. Runs

Cracking involves the formation of high-boiling substances as well as those of low boiling point. It must always be regarded in this dual sense. However, there is no organic analytical procedure that permits exact or even approximate estimation of all the products of the cracking reactions. Hence, the yield of 437° F. end-point distillate was used, inasmuch as this was a measure of the yield of the product commercially desired.

Little "coke" was formed in any run, although more was deposited when cracking the heavy fuel oil than when handling the other two oils.

Effect of Temperature on Rate of Cracking

As already indicated, the apparatus used in these experiments is so designed as to eliminate superheated oil films and to cause cracking to proceed throughout a uniformly heated homogeneous body of oil. Failure to recognize the fundamental importance of working in this manner is responsible for most of the irreconcilable results reported in the literature of cracking. If heat is flowing through the walls of a vessel in which cracking is proceeding, it is not sufficient to characterize the results by stating the temperature of the bulk of the oil. The rate of heat flow, which determines the temperature gradient in the film of superheated oil next the wall of the cracking vessel, is of equal importance. However, evaluation of the heat-flow rate is difficult. The necessity for its measurement can be avoided by use of an essentially adiabatic or balanced heat-flow bomb.

It may be noted that in oil cracking most of the so-called catalytic effects of one surface or another are nothing but the superheated film at work. The surface of any cracking vessel soon becomes coated with a layer of "coke," or material rich in carbon and poor in hydrogen, thus losing any possible initial catalytic activity. That coke itself is without positive catalytic effect is apparent when it is considered that the presence of even an extremely thin layer is sufficient materially to reduce the rate of cracking in an externally heated vessel. The presence of the carbonaceous layer reduces the rate of heat transfer and thus decreases the temperature of the superheated oil film. Slower cracking is the result.

The results of a series of experiments in which the gas oil, heavy fuel oil, and thermolized gas oil were heated for different lengths of time at 700° and 800° F. are summarized in Table II. The percentages given are all volumetric. "Gasoline in blank" refers to the gasoline contained in the sample taken at the start of each run. The "volume factor" is the ratio of the specific gravity of the oil charged to the bomb to the specific gravity of the cracked oil drawn from the bomb at the conclusion of the run. Use of this factor in the calculation results in basing all gasoline percentages on the oil charged to the bomb. When little cracking occurred the volume factor was 1.0, in which event the volume factor column is omitted from the table.

Table II—Rate of Gasoline Formation

Run	Time of run Min.	Av. temp. ° F.	Gasoline in blank Per cent	Gasoline in cracked oil Per cent	Volume factor	Gasoline made Per cent	Gasoline cor. Per cent	Unsaturateds Per cent
			Fractionated Gas Oil					
			Temperature, 700° F.					
88	30	690	9.6	10.0	...	0.4	0.5	...
87	60	698	9.4	10.3	...	0.9	1.0	...
91	90	697	9.6	10.6	...	1.0	1.2	...
89	150	695	10.4	12.8	...	2.4	2.6	...
81	212	700	9.0	12.7	...	3.7	3.7	...
90	300	698	9.5	15.2	...	5.7	5.8	...
82	303	700	9.3	16.4	...	7.1	7.1	...
85	461	700	9.1	19.4	...	10.3	10.3	...
			Temperature, 800° F.					
96	30	795	15.2	25.5	1.00	10.3	10.9	15.4
94	49	797	14.0	27.2	1.01	13.5	14.0	14.4
120	59	805	10.7	28.4	1.01	18.0	16.5	13.2
147	60	796	10.2	25.2	1.01	15.3	16.3	13.4
95	73	792	13.2	27.6	1.01	14.7	18.5	13.0
121	91	800	10.5	31.8	1.01	21.7	21.7	14.0
97	134	800	11.0	38.3	1.02	28.1	28.1	12.8
			Heavy Fuel Oil					
			Temperature, 700° F.					
104	30	698	10.5	11.2	1.00	0.7	0.8	...
105	60	699	10.4	11.3	1.00	0.9	1.0	...
102	90	698	6.7	8.0	1.00	1.3	1.5	...
103	150	699	7.0	8.7	1.00	1.7	2.0	...
101	210	699	7.0	9.1	1.01	2.1	2.5	...
100	300	700	6.3	10.7	1.01	4.4	4.4	...
			Temperature, 800° F.					
106	20	784	13.4	16.8	1.02	3.5	6.9	15.4
124	20	792	13.8	17.8	1.02	4.1	6.7	14.1
123	31	798	11.0	20.2	1.03	9.5	9.7	12.8
122	50	797	12.0	27.1	1.04	15.7	16.2	11.0
108	63	797	10.9	28.8	1.05	18.8	19.5	10.2
			Thermolized Gas Oil					
			Temperature, 700° F.					
135	60	709	7.2	6.8	1.00	−0.4	−1.0	14.0
134	120	699	7.0	4.8	1.00	−2.2	−2.2	13.0
133	180	698	8.3	6.8	1.00	−1.5	−1.4	10.6
132	300	700	9.2	8.0	1.00	−1.2	−1.2	10.4
			Temperature, 800° F.					
130	30	795	11.0	14.5	1.00	3.5	3.8	13.2
136	60	800	9.7	18.2	0.99	8.4	8.4	10.4
129	63	797	12.0	18.6	0.99	6.5	6.9	10.4
128	78	807	10.5	24.2	0.99	13.6	12.1	9.2
127	120	803	10.0	27.2	0.98	16.9	16.4	8.2

"Per cent of gasoline made" refers to the percentage actually made under the conditions of the run. The "per cent gasoline corrected" is the per cent of gasoline that would have been made had the average temperature during the run been 800° F. The temperature corrections of gasoline percentages were made by use of the curves of Figure 2. These curves were constructed by using data covering runs at 800° F. and at temperatures varying slightly from 800° F., the runs being of equal length. No temperature corrections, or only small corrections, were necessary when the cracking temperature was 700° F. because the rate of cracking was so slow.

The rate of cracking thermolized gas oil was only half that of the uncracked oils; hence the temperature corrections were only half those indicated in Figure 2.

The "per cent unsaturated" refers to the volumetric loss found when the distillate to 450° F. standard column vapor temperature was treated with 1.84 specific gravity sulfuric acid at 0° F. This is recognized as being a purely empirical measurement, but at least qualitatively indicative of the olefin content of the gasolines and therefore of some interest. No attempt was made to distinguish between the unsaturateds in the gasoline produced by cracking and those of the gasoline contained in the oil charged to the bomb.

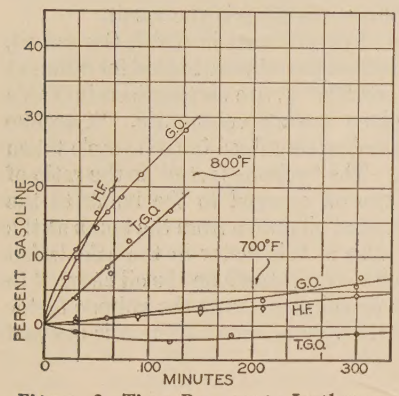

Figure 3—Time–Per cent Isotherms, No Vapor Removed

The extent of the cracking of each of the oils at 700° and 800° F. is shown in Figure 3. Several facts of importance are clearly illustrated.

The rate of cracking of gas oil and heavy fuel is slow at 700° F., but at 800° F. it is rapid. The approximate rule that the rate of a chemical reaction doubles for every 10° C. or 18° F. rise in temperature holds fairly well. The data indicate a doubling for every 12° C., or 22° F., when gasoline is formed from gas oil or heavy fuel oil.

The thermolized gas oil cracks in a negative sense at 700° F.; that is, less gasoline is contained in the "cracked" oil than in the thermolized gas oil used. This is a striking illustration of the fact that reactions of polymerization and condensation are concurrent with decompositions resulting in products of lower molecular weight than the oil treated. The thermolized gas oil was made from a Dubbs process residual oil, and therefore the hydrocarbons and other substances contained therein are presumably quite different from those of virgin gas oil or fuel oil. One would not expect extensive decomposition at 700° F., a temperature much lower than the cracking temperature used in the Dubbs plant. However, at 800° F. the thermolized gas oil cracks to form lower boiling substances, but at a rate only half that at which the heavy fuel cracks and materially lower than that at which gas oil decomposes.

These facts are of considerable importance in their bearing upon the use of "cycle stocks," or oils cracked once or more, as commercial charging stocks. If they are used, a rate of cracking roughly half that of new oil must be expected. However, the gasoline so made might conceivably be so olefinic and cyclic in character as to have valuable antiknock properties. This is indicated by the high specific gravity, as will be seen later.

The time-yield curves for gas oil and heavy fuel cross, both at 700° and 800° F. cracking temperature. Apparently, gas oil contains some substances of such molecular weight or character that scission results in two products of gasoline boiling range rather than one of low and one of high boiling point. This is more evident when working at 800° F. than at 700° F.

The time-yield curves, except for the 800° F. gas oil curve, are straight lines or substantially straight lines. It is evident, however, that had the reaction times been longer these curves would necessarily have shown a decreasing slope.

Originally, it was intended that a series of experiments would be made using a cracking temperature of 900° F. However, cracking was so rapid at 800° F. that runs at higher temperatures were practically out of the question. A run 10 minutes long at 830° F. resulted in the formation of 13.4 per cent of gasoline and caused the development of 1200 pounds pressure within the bomb.

Although the process of cracking is complicated because of the many substances present in the reaction mixture, it may be considered as involving scission of high molecular weight substances followed by recombination of part of the lower molecular weight substances to form substances of high molecular weight. The first reaction is of the first order and the second of the second order.

Considering cracking as a reaction of the first order, the reaction constants have been calculated. The equation may be written

$$\frac{X}{At} = K$$

in which

X = per cent gasoline formed
A = $(100-X)$ or the per cent of crackable material remaining
t = time in minutes
K = the reaction constant

Although, strictly speaking, a formulation of this character should be in terms of mols of the reacting substance and the product, this is quite out of the question in this instance. The molecular weights are not known.

Table III—Cracking Reaction Constants

Temperature 700° F.				*Temperature 800° F.*			
t	A	X	K	t	A	X	K
Fractionated Gas Oil				Fractionated Gas Oil			
30	99.5	0.5	0.000167	30	89.1	10.9	0.00407
60	99.0	1.0	0.000169	49	86.0	14.0	0.00332
90	98.8	1.2	0.000135	59	83.5	16.5	0.00335
150	97.4	2.6	0.000178	60	83.7	16.3	0.00324
212	96.3	3.7	0.000181	73	81.5	18.5	0.00311
300	94.2	5.8	0.000205	91	78.3	21.7	0.00304
Heavy Fuel Oil				134	71.9	28.1	0.00292
30	99.2	0.8	0.000269	Heavy Fuel Oil			
60	99.0	1.0	0.000169	20	93.1	6.9	0.00370
90	98.5	1.5	0.000169	20	93.3	6.7	0.00359
150	98.0	2.0	0.000136	31	90.3	9.7	0.00346
210	97.5	2.5	0.000122	50	83.8	16.2	0.00385
300	95.6	4.4	0.000153	63	80.5	19.5	0.00385
				Thermolized Gas Oil			
				30	96.2	3.8	0.00132
				60	91.6	8.4	0.00153
				63	93.1	6.9	0.00118
				78	87.9	12.1	0.00177
				120	83.6	16.4	0.00164

Inspection of Table III, in which the reaction constant values are given for the three oils, cracked at 700° and 800° F., shows that the formation of gasoline can reasonably be regarded as a reaction of the first order. The variation in value of the constant for gasoline formation at 700° F. is not greater than would be expected when it is considered that the amount of gasoline formed at this temperature was 0.5 to 5.8 per cent. An error of 0.5 per cent in the distillation analysis of either the blank or the sample would affect the net gasoline percentage 8 to 100 per cent.

The most reliable data are those for the cracking of heavy fuel oil at 800° F. The formation of gasoline was sufficient to permit accurate determination. The greatest variation of the value of the reaction constant is only 6.3 per cent from the mean value 0.00369. All the other values are within ±4.4 per cent.

Apparently the formation of gasoline from thermolized gas oil is essentially a first order reaction. Here again some of the actual gasoline percentages are low, and the chance of analytical error large. However, the values of the reaction constants for the two longest reaction times are in good agreement.

The cracking of fractionated gas oil presents the only real anomaly. The value of the reaction constant becomes less

as the reaction proceeds for a longer time; that is, gasoline is formed more rapidly initially than later. A possible and plausible explanation of this is that gas oil contains a considerable percentage of material of such boiling point that, if cracked, it would yield, not one, but two new molecules within the gasoline boiling range. Although this material may not be so reactive as that of high molecular weight, it nevertheless may contribute sufficient gasoline to cause the initial high formation rate. It will be noted that as cracking proceeds the reaction constant approaches a value of about 0.00300.

Effect of Pressure on Rate of Cracking

Pressure can have no effect on the initial scission of high molecular weight hydrocarbons. However, cracking, in the over-all sense, involves a succession of reactions, and pressure may conceivably influence such of these as form substances of high vapor pressure, and which, therefore, would form a large part of the vapor phase above the liquid in the cracking vessel. That the effect of pressure must be small in any cracking system in which the volume of the vapor phase is small, is evident when the relative densities of the vapor and liquid phases are considered. The weight of material present as vapor is small and hence the possible effect on the composition of the liquid phase is limited.

In considering the effect of pressure in these experiments it should be remembered that the oil was contained in an isothermal bomb. In commercial cracking practice pressure has an effect quite aside from a direct effect on the concentrations of reacting substances; namely, it influences the rate of vaporization and thus the heat flow rate and temperature of the superheated films. The literature contains a number of references to the effect of pressure on cracking. However, in no instance that has come to the writers' attention has pressure been oriented as the only variable factor and its effects as such determined.

In the first series of experiments to determine the effect of pressure the procedure involved the addition of nitrogen until the desired pressure was obtained. Nitrogen was chosen because it is inert. Had the pressure been built autogenously —that is, by the vapor of substances in the bomb—there would have been a change in the composition of the liquid phase commensurate with the weight of material necessarily converted from liquid to vapor in order to build the pressure.

The oils cracked were the fractionated gas oil and the thermolized gas oil. The heavy fuel oil cracked so rapidly that the rate of pressure rise was excessive. The pressure developed, when added to the nitrogen pressure, would have taxed the strength of the apparatus.

The results of four runs with each oil are summarized in Table IV. The column headed "Excess Pressure" gives the additional pressure impressed upon the contents of the bomb by means of admission of nitrogen. All runs were 60 minutes long.

Table IV—Effect of Pressure on Cracking

Run	Excess pressure Lb./sq. in.	Av. temp. °F.	Gasoline in blank Per cent	Gasoline in cracked oil Per cent	Volume factor	Gasoline made Per cent	Gasoline cor. Per cent	Unsaturateds Per cent
			Thermolized Gas Oil					
136	0	800	9.7	18.2	0.99	8.4	8.4	10.4
137	100	800	10.8	19.1	0.99	8.2	8.2	9.8
138	150	800	10.2	18.6	0.99	8.3	8.3	10.2
139	200	799	10.9	18.6	0.99	7.6	7.8	10.2
			Fractionated Gas Oil					
147	0	796	10.2	25.2	1.01	15.2	16.2	13.4
148	50	800	10.8	28.6	1.01	18.0	18.0	13.8
149	100	801	9.5	27.6	1.01	18.3	18.2	13.4
150	200	798	9.8	27.7	1.01	18.3	18.7	14.7

In a further series of experiments to determine the effect of pressure no nitrogen was added. The pressure was built by the decomposing oil and controlled at the desired total pressures by means of a regulated valve. The results are shown in Table V. As usual, corrections have been made for the volume factor and temperature variation. However, the scheme of operation necessitates a further correction because the vapor leaving the bomb during the run contains not only gasoline but high-boiling crackable substances as well. During the run the volume of distillate collected at various times was recorded. From these data and from the analysis of the distillate it is possible to calculate the volume of crackable oil in the bomb at any time and also the average volume present during the entire run. The next to last column in Table V gives the gasoline percentages so calculated.

Although the corrected gasoline percentage is indicated as increasing slightly with pressure, it is questionable if the increase observed can be justifiably considered as outside the limits of error of the experiments. Certainly it is so small as to be of no practical importance.

The percentages of "unsaturateds" as given in Tables IV and V show one point of interest. When no gasoline is removed from the bomb and the excess pressure is built with nitrogen, the per cent of unsaturateds is not affected. However, when gasoline is removed from the bomb the per cent of unsaturateds in the gasoline is affected by the total pressure in the bomb. This is apparently the result of the effect of pressure on the time that the gasoline formed remains in the apparatus, as well as upon the concentration of unsaturated substances in both the vapor and liquid phases. Increased concentration and longer time of heating both favor olefin condensation. There is no question but that increase of pressure decreases the percentage of olefins as determined by the sulfuric acid absorption test.

Another question that might be raised in this connection is the influence on the boiling range or distribution of compounds in the gasolines produced when operating under different pressures. That pressure as such has no effect can be seen from Table VI. It will be noted that the gasolines

Table V—Effect of Pressure on Cracking

Fractionated Gas Oil—Time 120 Minutes

(Vapor withdrawn at indicated total pressure)

Run	Pressure Lb./sq. in.	Av. temp. °F.	Gasoline in blank Per cent	Gasoline in cracked oil Per cent	Volume factor	Gasoline Per cent	Gasoline corrected for temperature variation Per cent	Gasoline corrected to basis crackable material present Per cent	Unsaturateds Per cent
99	200	800	13.3	38.7	1.02	25.9	25.9	31.0	17.8
112	300	799	11.2	36.5	1.02	25.8	26.0	30.1	14.6
145	400	800	11.0	42.5	1.02	32.1	32.1	33.7	10.8
146	500	800	13.5	46.4	1.02	33.8	33.8	34.1	10.4

The experiments show that pressure has no effect on the yield of gasoline from thermolized gas oil. The formation of gasoline from fractionated gas oil increases slightly with pressure, but the difference is so small as hardly to be considered as beyond the limits of experimental error. Surely it is of no practical importance.

are of a boiling range similar to products made from normal crude petroleum by a process of efficient fractionation.

A. S. T. M. analyses of the gasolines produced when excess nitrogen pressure was used in the bomb were also made. All

these gasolines were so closely alike that two different curves could hardly be drawn through the points.

Table VI—Effect of Pressure on Boiling Range of Gasoline
(A. S. T. M. 100-cc. distillations)

Pressure at which gasoline was removed from bomb / Per cent	200 lbs.	300 lbs.	400 lbs.	500 lbs.
F. D.	137	135	136	135
10	191	186	195	196
20	226	220	228	224
30	254	253	255	250
40	285	286	283	276
50	310	317	308	305
60	341	345	331	333
70	366	367	363	356
80	389	392	386	385
90	410	413	408	407
95	423	425	423	422
EP	436	437	436	438

Effect of Nature of Oil Cracked

The extent and rate of cracking of the three oils used in these experiments is given in Tables II and III and is illustrated in Figure 3.

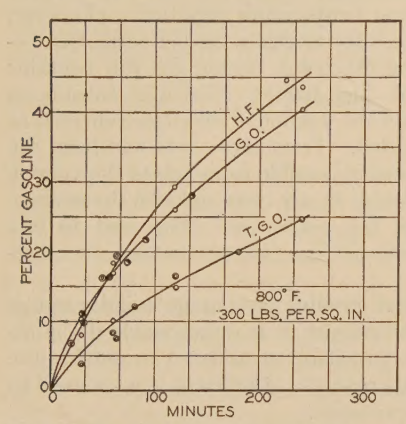

Figure 4—Time–Per cent 800° F. Isotherms with Vapor Removed

The fractionated gas oil contains some material of such boiling point as to yield two molecules of gasoline upon primary decomposition rather than one light and one heavy molecule. Hence, at 700° F. the fractionated gas oil yields more gasoline in any given time up to 5 hours than the heavy fuel oil. This is also true at 800° F., if the time of reaction is less than 40 minutes. However, fractionated gas oil does not crack more easily than heavy fuel oil, as is proved by the fact that at 800° F., except at the short times, the slope of the per cent–time curve is steeper for heavy fuel oil than for fractionated gas oil. The heavy fuel oil cracks most easily.

The thermolized gas oil at 800° F. cracks at a rate 0.4 that of the heavy fuel oil, or excluding the shortest times, at a rate 0.47 that of the fractionated gas oil. At 700° F. the polymerization reactions are more rapid than those of decomposition and the treatment of thermolized gas oil shows negative cracking.

Effect of Removal of Gasoline as Formed

A point of both theoretical and practical interest is the effect of removal or nonremoval from the cracking system of the gasoline formed. For example, in the Cross process no gasoline is removed during the cracking, whereas in the Dubbs process and in pressure-still processes gasoline is removed continuously.

If the reactions resulting in gasoline formation were reversible, the accumulation of gasoline in the cracking system would materially decrease the rate of gasoline formation. However, a condition of equilibrium is never even approached in cracking. The decomposition of high molecular weight substances to form substances of gasoline boiling range is uninfluenced either by accumulation or removal of gasoline, as can be seen from Figure 4. The curves are time–per cent 800° F. isotherms for the three oils used in this investigation, the gasoline having been removed as fast as formed. The pressure in the bomb was 300 pounds.

For comparison, the points given in Figure 3 are also plotted in Figure 4. These points represent the results obtained when the three oils and all reaction products were held in the bomb during the entire cracking period. Points for heavy fuel and thermolized gas oil are given as double circles, and those for the fractionated gas oil as half-moon circles. Points representing the results for removal and nonremoval of gasoline fall so closely on the curves for the three oils that the accuracy of the work would not justify construction of two curves for each oil.

The complete data are given in Table VII. Corrections have been made for temperature variation and for the volume factor, but not for the removal of crackable material along with the gasoline vapor. This latter correction would be desirable, but could not be made because the necessary data were not taken at the time of making the runs. The effect of this removal of crackable material is that the slope of the per cent–time curves decreases sooner than if all material had been retained in the bomb. The longer cracking times were possible at 800° F. when the low-boiling products were removed as formed.

Table VII—Rate of Gasoline Formation when Gasoline Is Removed as Formed
(800° F.; 300 pounds pressure)

Run	Time Min.	Av. temp. ° F.	Gasoline in blank Per cent	Gasoline in cracked oil Per cent	Volume factor	Gasoline made Per cent	Gasoline cor. Per cent	Unsaturateds Per cent
			Fractionated Gas Oil					
111	30	781	10.7	17.6	1.00	6.9	10.3	16.0
113	60	796	12.0	27.7	1.01	15.9	16.9	16.4
112	122	799	11.2	36.5	1.02	25.8	26.0	14.6
114	240	798	9.0	47.2	1.03	39.4	40.4	12.6
			Heavy Fuel Oil					
110	30	797	12.8	20.3	1.02	7.7	8.3	13.6
109	60	800	13.5	31.3	1.04	18.5	18.5	13.2
116	120	799	13.0	40.5	1.06	29.2	29.4	11.8
115	225	803	13.4	56.5	1.07	46.1	44.6	11.0
117	240	800	12.3	52.6	1.08	43.6	43.6	10.8
			Thermolized Gas Oil					
143	60	800	10.3	20.4	1.00	10.1	10.1	10.7
141	120	798	10.2	24.9	0.98	14.6	14.9	8.6
144	180	804	9.0	32.3	0.98	22.8	20.0	7.8
142	240	800	11.3	36.4	0.98	24.6	24.6	8.0

The conclusions stated above are in complete disagreement with those of Brooks[4] and his co-workers. These investigators found it necessary to remove gasoline as fast as formed. However, they do not give the temperature in the two cases. Clearly, removal of product was not the only variable involved in their work. The high per cents of gasoline formed without gasoline removal in the Cross process are a sufficient qualitative proof of the lack of necessity of gasoline removal. The results of experiments reported in this paper show quantitatively that removal is without effect.

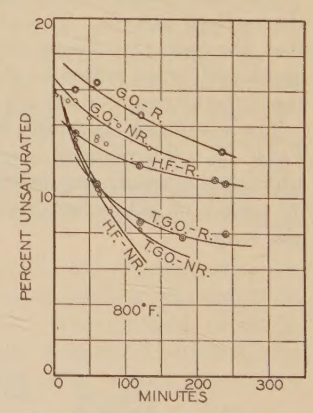

Figure 5—Unsaturation of Gasolines

It is not to be contended that gases and gasoline should not be removed from a cracking system. From the standpoint of decreased operating pressure this may be highly desirable. The removal factor, as such, is without effect on gasoline yield. However, indirect influences may be introduced by virtue of the return of the uncracked material to the cracking system. These must be carefully analyzed in each instance. Also, if the temperature of the reacting oil decreases through vaporization of gasoline it may seriously affect results.

One interesting effect of removal of gasoline as soon as formed is shown in Figure 5, in which are plotted the per

[4] THIS JOURNAL, **7**, 180 (1915).

cents unsaturateds in the gasolines made with and without removal of gasoline as formed. The curves designated R and NR are for removal and nonremoval. In every instance the unsaturateds are present in larger proportion in the gasolines made by the process of removing the gasoline as formed. The reason for this has already been discussed.

A further point of interest is that the unsaturation of the gasoline decreases with time of cracking, indicating a continuing polymerization of the more reactive olefins.

Rate of Pressure Rise in Cracking

The absolute and comparative rates of pressure rise during cracking of the three oils are shown in Figure 6. The per cent of gasoline formed and the rate of pressure rise do not run entirely parallel, for the average molecular weight of the original oil and the nongasoline material formed on cracking, as well as the gasoline formed, influence the pressure rise.

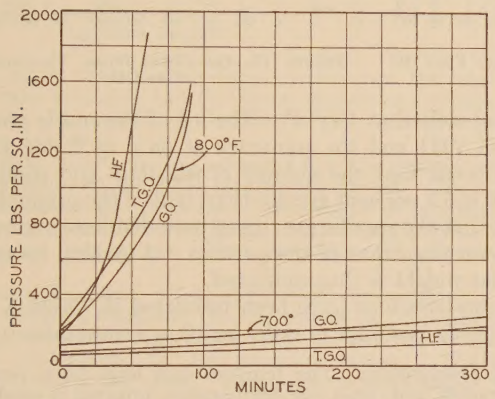

Figure 6—Rates of Pressure Rise in Cracking

In addition to giving information as to what actual pressure develops when oils are cracked at 700° and 800° F., Figure 6 illustrates the fact that equilibrium is not attained. Molecular decomposition and polymerization both proceed, but the net result is more molecules the longer the time.

Relationship of Specific Gravity and Extent of Cracking

In Figure 7 the time of cracking is plotted against the specific gravity of the cracked oil formed in the given time. The data here presented are for those experiments in which all of the oil was held in the bomb under the pressure developed by the cracking of the oil itself. The cracked thermolized gas oil has the highest specific gravity, cracked heavy fuel is next, and the cracked gas oil lowest. Although the specific gravity of the cracked oils from gas oil and heavy fuel decrease with increased time of cracking, the specific gravity of the thermolized gas oil increases, and this notwithstanding the large increase in the gasoline content of the cracked thermolized gas oil. The marked effect of the polymerization reactions is thus evident.

The relationship of specific gravity of the cracked oils to the gasoline content of the cracked oils is shown in Figure 8. The marked contrast between the gas and heavy fuel oils and the thermolized gas oil is illustrated.

The mean specific gravities of the gasolines produced from the three oils are as follows:

Source	Specific gravity (60°/60° F.)
Gas oil	0.7790
Heavy fuel	0.7693
Thermolized gas oil	0.7873

The gasoline from the thermolized gas oil is apparently the most cyclic in character and presumably would therefore have the best antiknock characteristics.

Character of Gasoline Produced by Cracking

Successful cracking presupposes not only a large yield of gasoline but also the production of a gasoline of proper boiling range. In order to ascertain the boiling range, or the distribution of components, in the material boiling below 450° F. made in these experiments, the distillation curves of the products have been corrected for the material of the same boiling range contained in the blank sample. The A. S. T. M. distillation curves of the material of gasoline boiling range actually produced during the cracking times indicated are shown in Figures 9, 10, and 11 for gas oil, heavy fuel oil, and thermolized gas oil, respectively.

In cracking each oil the character of the gasoline distillate changes with the time of cracking in the sense of becoming richer in the more volatile substances. At any given time the volatility of the gasoline from the heavy fuel oil is best, from gas oil intermediate, and from thermolized gas oil worst.

The characteristics of the gasolines produced in those experiments in which the gasoline was removed as formed were also studied. Removal of the gasoline had no effect on the boiling range of the final product. The relationships between time and boiling range of the gasolines are so similar to those illustrated in Figures 9, 10, and 11 as to render reproduction of the curves unnecessary.

The effect of pressure on the quality of the gasoline has already been discussed and shown to be negligible.

Thermal Relations in Cracking

A question of very real importance in commercial cracking operations is that of the thermal change resultant from the over-all process of cracking. Is heat absorbed or liberated during cracking? Opinions have been expressed both ways, but no experimental evidence has been presented as a basis for these opinions.

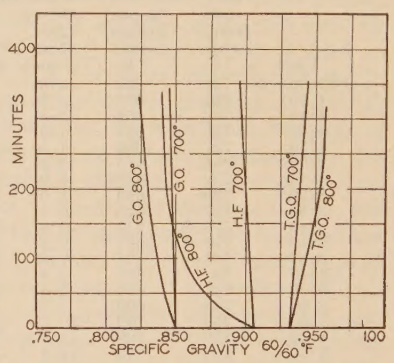

Figure 7—Specific Gravity of Cracked Oils

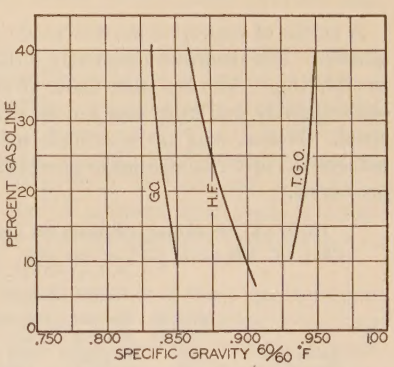

Figure 8—Specific Gravity of Cracked Oils as Related to Gasoline Formed

The operation of the bomb in these investigations proves, at least qualitatively, that heat is absorbed in cracking. The bomb was maintained at 800° F. during the cracking period by radiation from resistance coils on the inner surface of the insulating jacket. At the conclusion of an experiment the oil was blown from the bomb. The temperature started to rise at once, although the bomb wall was only 10° F. or less above the temperature of the oil, and continued to rise until, in 15 minutes, the temperature was about 830° F. This phenomenon was observed in each experiment.

However, it was desired to obtain data, of at least a rough quantitative nature, as to the heat absorption during cracking. The apparatus shown in Figure 12 was arranged. A round-

bottom Pyrex glass flask, *A*, was immersed in a box of powdered Sil-o-Cel, *B*, and heated by a resistance coil, *C*, immersed in the oil. The voltage drop across the coil and the current flowing were measured by precision voltmeter and ammeter, *D* and *E*. A small high-speed propeller, *F*, stirred the oil violently. The shaft of this stirrer was made of glass to minimize the heat loss by conductance. The heat of stirring was measured and found to be negligible in these experiments.

beginning of the aluminum chloride run, at which time heat was evolved as a result of the combination of the oil and aluminum chloride.

In the last run, in which the technic was best developed, paraffin wax was cracked. This material presents one further advantage for this particular purpose—namely, it contains no low-boiling hydrocarbons and probably fewer higher hydrocarbons than any of the other materials used. The

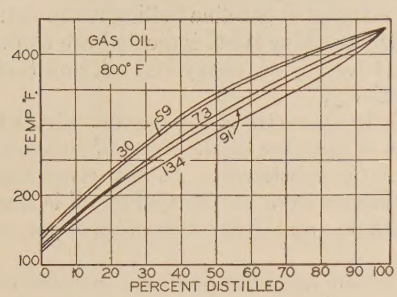

Figure 9—Gasolines from Gas Oil

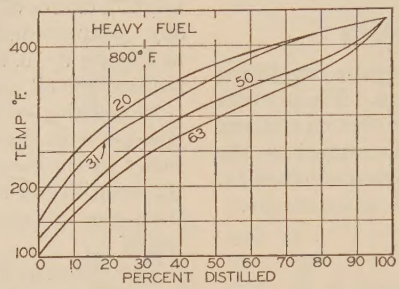

Figure 10—Gasolines from Heavy Fuel Oil

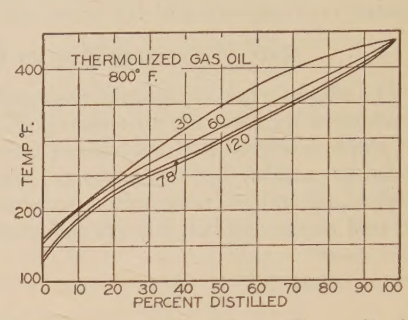

Figure 11—Gasolines from Thermolized Gas Oil

During an experiment the oil was heated by means of the immersed coil. The temperature was taken by means of thermometer *I*. Vapor was evolved and its temperature taken by thermometer *H*. The vapor was condensed in *J* and weighed as collected as liquid.

Table VIII—Log of Cracking Paraffin Wax

Time	Oil temperature °F.	Vapor temperature °F.	Wt. of distillate Grams	Wt. of total distillate Grams	Voltage	Amperage
12:50 P. M.	736	683	4.0	32.0		
1:00	732	673	2.0	34.0		
1:10	730	658	2.5	36.5	15.3	3.02
1:20	728	651	1.0	37.5		
1:30	727	639	1.5	39.0		
2:00	736	675	2.5	56.5		
2:10	732	656	2.0	58.5		
2:20	730	640	1.0	59.5		
2:30	727	625	0.5	60.0	17.0	2.52
2:40	726.5	617	0.3	60.3		
2:50	725.5	612	0.2	60.5		
3:30	747.5	695	7.0	97.0		
3:40	747	693	5.8	102.8		
3:50	746	691	4.6	107.4	19.0	2.81
4:00	746	690	3.7	111.1		
4:30	758	709	20.0	155.0		
4:40	759	709	13.3	168.3		
4:50	760	713	12.4	180.7	20.3	3.03
5:00	760	711	10.9	191.6		
5:10	760	710	9.4	201.0		

A series of experiments was made using different charging stocks. The results consistently indicated absorption of heat in cracking. All runs were made at atmospheric pressure and consequently cracking was not so extensive as might be desired. Hence, one run was made using aluminum chloride as catalyst in order that a large percentage of gasoline might be produced.

Table IX—Summary of Data on Cracking Paraffin Wax

Charged: 499 grams (557 cc.) paraffin. Specific gravity, 0.8957; ° A. P. I. at 60° F., 26.5

Yield Distillate

	Weight Grams	Specific gravity	Volume Cc.	Per cent by volume	° A. P. I. at 60° F.
Distillate	201	0.7886	255	45.8	47.9
Residue	290	0.8623	336	60.3	32.6
Loss	8	...	...	...	...

Yield Gasoline

Charged: 45.8 per cent distillate (255 cc.)

	Volume Cc.	Distillate Per cent by volume	Charge Per cent by volume	° A. P. I.
Gasoline	52	20.4	9.4	59.8
Residue	201	78.8	36.1	43.3
Loss	2	0.8	0.4	...

The logs and calculations of these runs are so voluminous as to preclude their inclusion here. However, results of all runs were in conformity with those of the one for which data are presented. The only exception to this was in the very wax used melted at 130° F. The log of the run is presented as Table VIII and the summary of data as Table IX. It will be noted that the volume of distillate and residual oil together is 6.2 per cent greater than that of the original paraffin, and that the specific gravity of both distillate and residual oil is lower than that of the paraffin. A general lowering of molecular weight is thus indicated.

The computations have been tabulated in Table X under the following headings in order to allow computation:

Mean Temperature. The temperatures have been converted to Centigrade and, since the temperature interval is small in all cases, the arithmetic average for any interval is close to the true mean.

Radiation. To determine the amount of heat radiated as a function of temperature, the following procedure was adopted: The bottle was filled with an equimolar mixture of fused sodium and potassium nitrates. This liquid was selected because it was necessary to have a liquid that was thermally stable at the temperature in question. Heat was supplied by means of an enclosed heater and the system allowed to stand until thermal equilibrium was reached. At this point all the heat supplied was being radiated. In this way a curve was obtained, making it possible to read directly the radiation at any temperature.

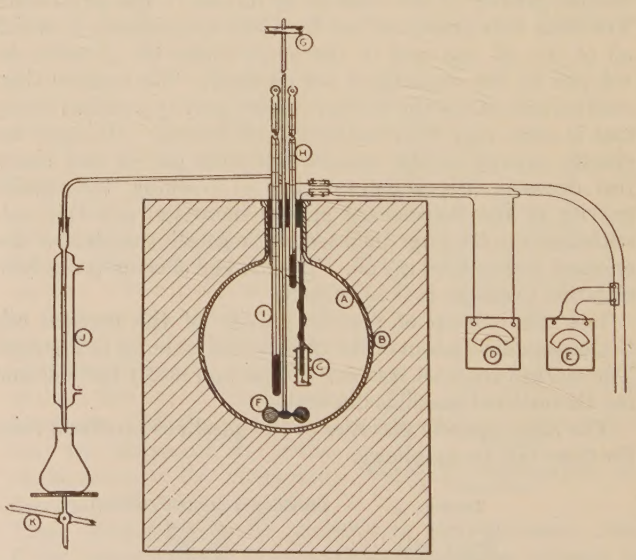

Figure 12—Apparatus for Studying Thermal Relations in Cracking

Temperature Interval. Difference between the initial and final temperature converted into degrees Centigrade.

Specific Heat of Glass. Although the specific heat of all sub-

Table X—Summary of Computations for Cracking Paraffin Wax

Mean temp., ° C.	Radiation, cal. in 10 min.	Temp. interval, °C.	Specific heat of glass	Heat into glass, cal.	Grams of distillate	Total weight of distillate, grams	Weight of oil in flask, grams	Latent heat of distillate	Heat of vaporization, cal.	Specific heat of residue	Heat into oil, cal.	0.24 EIT	Heat absorbed, cal.	Cal. absorbed per gram of gasoline formed
392.7	6070	3.3	0.34	−232	4	32.0	467.0	35	140	1.09	−1680	6700	2402	7,500
390.0	6000	2.2		−155	2	34.0	465		70		−1115	6700	1900	11,880
388.4	5970	1.7		−120	2.5	36.5	462.5		88		− 856	6700	1718	8,590
387.2	5940	1.1		− 78	1.0	37.5	461.5		35		− 554	6700	1357	16,960
386.6	5930	0.6		− 42	1.5	39.0	460.0		53		− 301	6700	1060	8,830
390.0	6000	2.2		−155	2.0	58.5	440.5		70		−1053	6160	1298	8,120
388.4	5970	1.7		−120	1.0	59.5	439.5		35		− 814	6160	1089	13,600
387.0	5940	1.1		− 78	0.5	60.0	439.0		18		− 526	6160	806	20,160
386.1	5920	0.6		− 42	0.3	60.3	438.7		11		− 287	6160	558	23,200
385.6	5900	0.3		− 21	0.2	60.5	438.5		7		− 144	6160	418	26,150
398.3	6190	1.1		− 78	7.0	97.0	402.0		245		− 481	7690	1814	3,220
397.2	6170	0.6		− 42	5.8	102.8	369.2		203		− 88	7690	1447	3,120
396.7	6160	0.0		0	4.6	107.4	391.6		161		0	7690	1369	3,720
396.7	6160	0.0		0	3.7	111.1	387.9		130		0	7690	1400	4,730
402.8	6300	1.1		78	18.8	155.0	344.0		658		413	8850	1401	933
403.1	6330	0.6		42	13.3	168.3	330.7		465		223	8850	1790	1,682
403.4	6332	0.6		42	12.4	180.7	318.3		435		208	8850	1833	1,850
404.4	6340	0.0		0	10.9	191.6	307.4		382		0	8850	2128	2,440
404.4	6340	0.0		0	9.4	201.0	298.0		329		0	8850	2181	2,900

stances varies with temperature, in this case the uncertainty of the data available and the short temperature ranges render additional refinements of doubtful value. An average value only has been used.

Heat into Glass. It was assumed that the entire bottle rose in temperature at the same rate as did the oil. The values in this column are the products of the weight of the bottle (207 grams), the specific heat of glass, and the temperature interval. The rise in temperature of the insulating Sil-o-Cel was neglected.

Grams of Distillate. Obtained directly by weighing.

Total Grams of Distillate. Summation of the preceding column.

Weight of Oil in Flask. Difference between the weight of oil charged (499 grams) and the preceding column. The gas loss was less than 2 per cent. Therefore, no appreciable error is introduced by subtracting these two values.

Latent Heat of Distillate. No experimental data exist for the temperature range used in the experiment, but extrapolation of the existing low temperature data is fairly concordant, so an average value has been selected. The latent heat is known to vary with the molecular weight, but since the data available are not precise, and the amounts distilled were not large, no large error is introduced by using an average value.

Heat for Vaporization. Product of the preceding column and the weight of distillate.

Specific Heat. As in the case of latent heat, the data in the literature are neither precise nor consistent. An average value has again been selected with the same precautions applying.

Heat into Oil. Product of the weight of oil, the specific heat, and the temperature interval. When the system is cooling, the heat into the oil has been denoted as negative.

0.24 EIT. Total heat added to the system by means of the heating coil.

Heat Absorbed. Amount of heat absorbed by the oil in changes other than distillation, increase in temperature, and radiation.

Calories Absorbed per Gram of Gasoline Formed. Figures obtained by assuming that the distillate contained 8 per cent by weight of gasoline and that all of the heat absorbed was chargeable to this amount of gasoline.

It will be noted that when all of the heat absorbed during cracking is charged to gasoline formation the calories per gram of gasoline vary widely. This has been observed in all experimental runs, and is particularly true of the oils of most diverse composition and highest average molecular weight. Decomposition, depending on conditions, may result in gasoline formation or in formation of substances of higher molecular weight than gasoline. Hence, the wide variations in calories absorbed per gram of gasoline formed. All the other runs substantiate the results of this run in this connection.

In the run using aluminum chloride, from 550 to 1000 calories were absorbed per gram of gasoline produced, when removing a distillate containing 55 to 75 per cent of gasoline. It therefore appears logical to assume that in this reaction not more than 500 calories were absorbed for each gram of gasoline produced. All the cracking distillation runs would point to approximately the same figure if it were possible to exclude the crackable material from the distillate. When more heat is absorbed than 500 calories per gram of gasoline produced, it indicates that conditions are such that gasoline is a minor product of the over-all process of cracking.

If the heat of reaction required to produce 1 gram of gasoline is assumed to be 500 calories, or 900 B. t. u. per pound, and 30 per cent of gasoline by volume, or 26 per cent by weight, is produced by cracking, the absorption of heat in cracking would be 234 B. t. u. per pound of stock cracked, or enough to lower the temperature of the cracking oil 215° F. This appears to be fairly well in line with what happens in the Cross process, in which part of the cracking occurs in the tubes and part in the reaction chamber. Although the reaction time in the tubes is small, the temperature of the bulk of the oil is high and that of the superheated film next the tube surface 100° to 150° F. higher. This must result in rapid cracking. If half the cracking occurs in the tubes and half in the reaction chamber, as appears to be reasonable, the difference in temperature between the oil in the transfer line to the chamber and the oil exiting from the chamber should be approximately 100° F., based on the above data for heat absorption in cracking.

The absorption of heat in cracking explains why cracking appears to proceed so far and no further in a process such as the Cross, in which the reaction proceeds in a well-insulated but unheated chamber. It is not a question of reaching an equilibrium state, but rather one of the decreasing reaction rate resulting from the absorption of heat and decreasing temperature. A drop of 100° F. means that the rate of cracking is only one-thirtieth as great at the lower temperature as at the higher.

Although recognition of this point is of very great importance in considering the manner of engineering a cracking process, the actual heat quantity involved is small in comparison to the total heat used in the cracking operation. In the laboratory system under consideration (insulated bottle), which is extremely favorable for minimizing the heat losses, a greater portion of the heat is lost by radiation. At 760° F., out of 8850 calories introduced, 6340 calories, or 71.6 per cent, are lost in radiation and conduction and are not available for cracking in any way. The remaining 28.4 per cent of the heat must do all of the cracking and distillation. Evidently, efficient insulation of the entire cracking still is most important, for this is the point at which heat economies might be most easily made. Further than this, the greatly decreased reaction rate at the lower temperature

resulting from heat loss, either by absorption in cracking or by radiation, suggests the advisability of heating reaction chambers, at least sufficiently to balance radiation and possibly sufficiently to make up for the heat absorbed in cracking itself. This point has apparently been generally overlooked.

Acknowledgment

The writers wish to acknowledge their indebtedness to E. B. Badger & Sons Co., Boston, Mass., for without the facilities available to them at the Petroleum Experimental Station of this company, located at Ann Arbor, Michigan, this investigation would not have been made.